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AN ULTRASONIC MOLECULE-SMASHER

DR. ALFRED WEISSLER, Directorate of Chemical Sciences, AFOSR

The mysterious shattering of a wineglass by a violinist's high note is similar, in some ways, to the shattering of molecules by intense ultrasound. Currently, a better understanding of the chemical effects of ultrasound waves is being achieved through the AFOSR-supported research of Dr. Douglas L. Currell at Los Angeles State College. Among the known effects of ultrasound in liquids are depolymerization, polymerization, oxidation, reduction, and disruption of molecules such as water or carbon tetrachloride.

In the specific case of the ultrasonic splitting of ring compounds like benzene, phenol, and pyridine into acetylene and other products, Dr. Currell has found that the surface tension and pH of the solution, and the nature of the dissolved gas, all affect the results significantly.

Another sonochemical reaction under scrutiny by this investigator is the disintegration of organic halides in aqueous suspension in the presence of argon, again with the production of acetylene and also hydrogen halide. Even the saturated hydrocarbon, n-decane, yields small amounts of acetylene upon ultrasonic irradiation in aqueous suspension. The consistent formation of this highly endothermic product (acetylene) points up the extreme concentration of energy which takes place in the ultrasonic wave, as a result of cavitation.

"Cavitation" refers to the formation and violent collapse of voids in the liquid, as a result of pressure alternations in the sound wave. In the typical case of water saturated with air, during the negative pressure phase some of the dissolved air comes out of solution as minute bubbles, which act as weak spots for the further tearing-apart of the liquid. Then, in the positive pressure part of the cycle, the cavities collapse violently with the generation of local temperatures close to 10,000°. Under these conditions, some molecules are broken up into free radicals, which then undergo further reactions. The entire process may be repeated millions of times each second, giving rise to appreciable amounts of hydrogen peroxide and nitrous and nitric acids. If cavitation is prevented by careful degassing of the water, the chemical reactions vanish.

These studies represent one aspect of the overall fundamental problem of the interaction between energy and matter; they also have practical importance. Already, sonochemical reactions are being used in analytical chemistry and in monitoring ultrasonic cleaning equipment. For the Air Force, it is necessary to know whether the intense sound fields near jet engines and rockets cause deterioration of materials, or interference with biochemical processes in the pilot.

TO OUR READERS

The continuing goal of the "OAR RESEARCH REVIEW" is an attempt to satisfy the information needs of both the scientist and the nonscientist decision maker, since we feel each is of importance.

It is inevitable that many decisions concerning basic research, from the budget that supports it to the manner in which it is fed into applied research and development activities, are made by people who are not scientists.

We believe that it is imperative that these people be informed about research in progress, and understand something of its potentialities. It is equally imperative that the scientist be kept up to date on research projects occurring within his areas of interest. Each time this publication prevents needless duplication of effort by informing a research scientist of new knowledge discovered, it will have achieved an important contribution of the Free World's scientific resources.

Those of you among our readers who feel a need for further information about a topic covered in any issue are urged to contact the author or originating laboratory direct. Addresses for use on such occasions are shown on inside back cover of this issue.

Constructive criticism and suggestions for improvement will be most welcome, and should be directed to this headquarters, ATTN: RREI.

Daniel E. Hooks

DANIEL E. HOOKS
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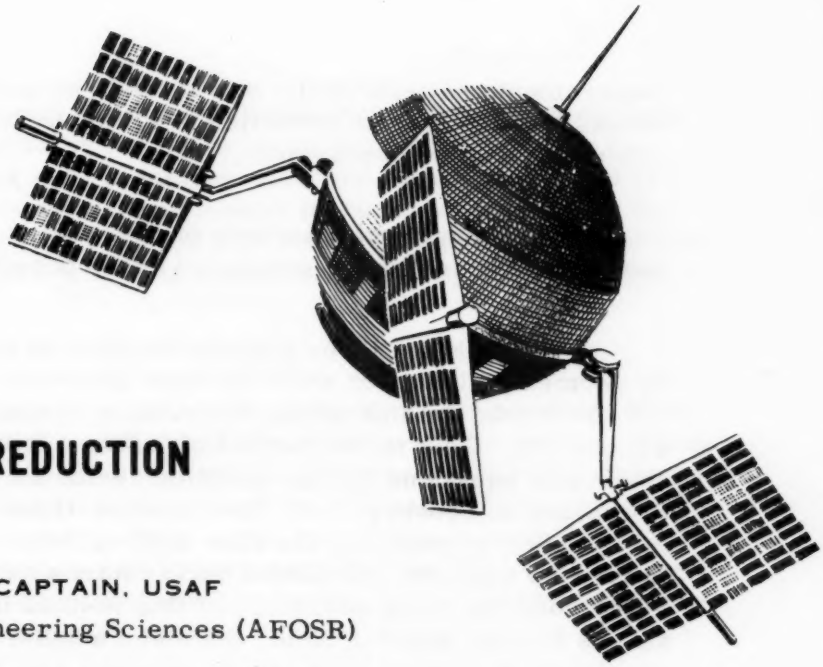

PRECISION ORBITS and OBSERVATION REDUCTION

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With the launching in increasing numbers of artificial satellites and space probes, the need for stream-lined methods of high accuracy orbit determination has been widely recognized. There was need for making available to students a clear exposition and systematic appraisal of the classical methods of deriving orbits and for adapting these methods to the new practical problems introduced by probes, satellites and interplanetary vehicles. In consideration of the importance of such an investigation, AFOSR Contract No. 49(638)-498 was granted to UCLA in 1959, to be administered by Dr. Samuel Herrick, whose long experience in both theoretical and practical problems makes him a leading authority in Astrodynamics.

In Astrodynamical Report No. 1 (AFOSR TN 59-769), Dr. Herrick discusses (a) the observational basis of precision orbits; (b) orbit improvement by differential correction; (c) the provinces of the observer and orbit analyst in reducing the observations to the center of the Earth and other adjustments; (d) generally useful reference systems; and (e) a comparison of fundamental orbit procedures.

With regard to coordinate systems, he points out the superiority of the equatorial over the ecliptic system of classical celestial mechanics, particularly for geocentric orbits. He does not recommend the proposed use of the "invariable plane of the solar system," first, because the well-established equatorial system meets all

requirements satisfactorily; and second, because the change would necessitate the tedious reduction of all published stellar and planetary coordinates to the new system.

Four fundamental methods of deriving an unperturbed or two-body reference orbit are compared and reduced to two:

(1) From three position vectors an orbit may be determined by geometry alone; but when the time intervals or dynamical relations are taken into consideration, the orbit is overdetermined and requires adjustment. This is the method of Willard Gibbs. Gauss substituted dynamical equations for one position vector and sacrificed simplicity to rapidity of convergence. The Herrick-Gibbs procedure, based on two position vectors and the time interval between them is adapted to modern machine calculation and requires successive approximations in the solution. One advantage of this method is that, if the two positions are far apart in time, the mean angular motion, period of revolution and major axis can be obtained with high accuracy.

(2) From one position vector and the velocities and accelerations of the components the orbit may be derived geometrically. The solution is greatly strengthened, however, by introducing the equations of motion, instead of deriving the acceleration vector from the observations (e.g., by Taylor's series) and the process is greatly simplified at the same time. This is the method of Lagrange and Laplace. It is a direct solution, but has the disadvantage that the velocities cannot be observed as accurately as the coordinates, at present.

In the light of astrodynamical experience, Dr. Herrick critically examines certain proposals which have appeared in print since the beginning of the Space Age. With regard to the belief that observations should be made in instantaneous sets comprising three components of the position vector and three of the velocity vector, he points out that any observed quantity is usable if it is sufficiently accurate, whether it is part of a "complete fix" or not.

To the suggestion that triangulation should be used to combine instantaneous observations made at several stations, when it is not possible to make all the observations at the same station, he replies

that there is no necessity for such a combination. The observational data should be submitted by the observer to the orbit analyst in its original state, subject only to instrumental and local corrections (e.g., refraction) by the observer. It is always more effective to apply dynamical relations between observations rather than purely geometrical ties, whether the object is to obtain position, velocity, acceleration or an orbit.

The responsibility of combining a great many observations from all over the globe into an orbit correction rests with the analyst, whose first act is to reduce the observations to a common geocentric system by rotating the topocentric axes through the co-latitude, longitude and sidereal time of the station. This is the simplest and most direct method of treating the data and is preferable to proposed methods involving the "subsatellite point" and " reduction to the geoid," which introduce unnecessary uncertainties.

To make a differential orbit correction, the analyst must then "represent the observations"; i.e., he must compare the predicted and the actual positions to obtain the "residuals." These form the basis for adjusting the orbital elements so as to obtain a better fit of the observed path. The success of this procedure depends on the accuracy of the observations. As each component of a position or velocity vector yields a residual, it is not at all necessary to work with complete fixes.

Dr. Herrick emphasizes the fact that the need for the highest observational accuracy highlights one problem that must be solved for continuous-thrust orbit theory (e.g., as encountered with low-thrust ion motors) and for low altitude satellite theory. In the absence of continuous thrust and uncertain drag effects the basic theory is good to 10^{-6} or more. This accuracy equals that of the observations, and so makes it possible to obtain residuals of the necessary precision. From the introduction, however, of continuous thrust or drag into the theory arise uncertainties that may be of the order of 10^{-3}, thus reducing the accuracy by a large factor. The problem, Dr. Herrick concludes, evidently requires investigation in two areas: in thrust controls, and in a new kind of perturbative theory. Theoretical investigations in these directions may prevent costly mistakes.

a high temperature high density *HYDROGEN PLASMA*

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In recent years, the physics of high temperature plasmas has attracted wide scientific interest in view of possible applications in space flight, propulsion and simulation of reentry conditions. Technical developments already under way are in many cases not backed up satisfactorily by fundamental research. It has to be conceded that the knowledge of the nature and the behaviour of plasmas is still rather incomplete.

One of the more common methods of generating a high temperature plasma is the electrical arc discharge. The column of the arc represents a plasma of rather high density which consists of a mixture of neutral and excited molecules and atoms, ions, electrons and photons at high temperature. There exists a very vigorous interaction among the constituents of the plasma. For the complete description of a plasma, various parameters have to be determined. One of the most important parameters is the temperature. Knowing the temperature at every point in the plasma, one can derive other significant properties of the plasma, such as the degree of ionization, the electrical and the thermal conductivity, and the viscosity.

Plasmas having temperatures above 10,000 degrees Kelvin preclude the use of conventional temperature sensing devices. These plasmas, being strong sources of radiation, suggest the use of spectroscopic methods. The radiation emitted is primarily a function of density and temperature. The question of whether there is a local thermal equilibrium among the plasma components, especially the ions, electrons and neutrals, is of paramount importance for the correct interpretation of the radiation. Local thermal equilibrium can exist in a plasma only if the macroscopic electric field intensity is zero. If an electric field exists, if feeds energy primarily to the electrons which have the highest mobility among the carriers of current in the plasma. By collisions, the electrons in turn transfer energy to the heavy particles. By this mechanism, a temperature difference between the electron temperature and the temperature of ions and neutrals is established. Because an electric field and current exist in the arc plasma, complete local thermal equilibrium

cannot be achieved. Only with very small field strengths and high densities is the assumption of local thermal equilibrium permissible. A significant energy loss by radiation also disturbs the thermal equilibrium.

Many fundamental questions, yet to be answered, arise from plasma diagnostics. To study and hopefully answer some of these, the Plasma Physics Research Laboratory of the Aeronautical Research Laboratories decided to start its experimental program with an arc plasma. For the planned investigations, a plasma generated under well-controlled conditions is needed. Of primary importance are the absence of contaminations stemming from evaporating electrode and wall materials and the geometry of the plasma. For ease of interpretation, a gas to which the fundamental atomic theories can be applied without restrictions should be used. Hydrogen fulfills this requirement but creates other experimental difficulties. With the spectroscopic instrumentation in mind, an arrangement had to be found which permits the unobstructed viewing of the plasma column. Based upon previous experience obtained at the Institute for High Temperature Research of the Technical University of Stuttgart, Germany, a new arc device (Fig 1) has been developed which employs

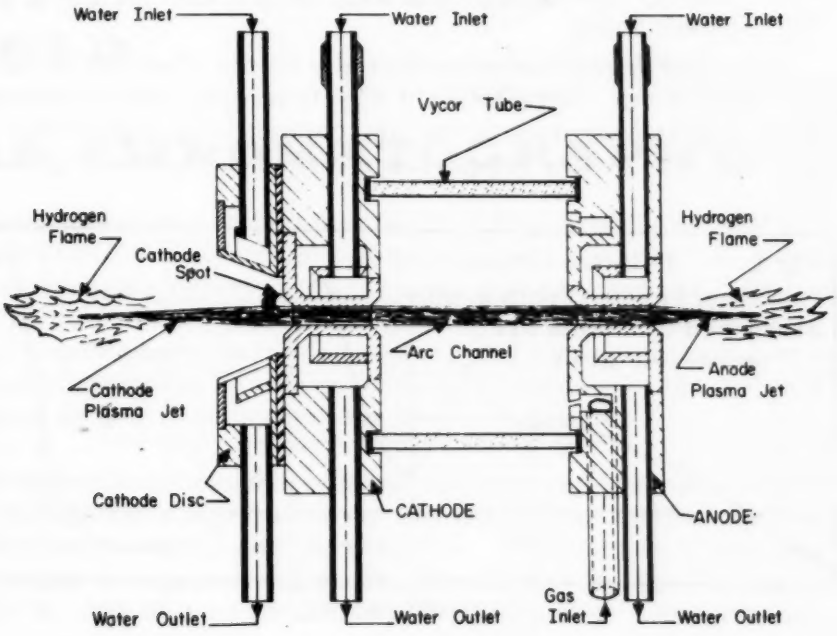

Fig 1. Hydrogen Arc - vortex chamber

a vortex for the stabilization of the arc column. The gas (hydrogen) enters the discharge chamber in a tangential direction at the anode end forming a vortex and escapes through small central holes in the electrodes. By means of the strong vortex, the arc column is confined to the axis of the chamber. An essential feature of this design is that the cathode spot of the discharge forms at the outside of the chamber. Thus, particles resulting from cathode erosion which takes place in spite of intensive water cooling are kept out of the discharge chamber. No lines traceable to the electrode metal (copper) have been detected in the spectrum. During operation, plasma jets escape through the holes in both electrodes. The length of these jets is a function of the electrical current and of the flow conditions of the stabilizing gas. The temperature in the jets decreases very rapidly with the distance from the exit holes.

In order to study the energy dissipation mechanisms in the hydrogen arc, energy balance measurements have been performed. With a power input of 70 KW the following results have been obtained:

Energy transferred to the hydrogen gas 85%

Energy lost to the electrodes 13%

Energy losses by radiation ..... 2% of the power input.

The experiments were conducted with the chamber pressure slightly above 1 atm. Preliminary spectroscopic measurements indicated the axis temperature of the arc column to be higher than 20,000 degrees Kelvin. At this temperature level the plasma is almost

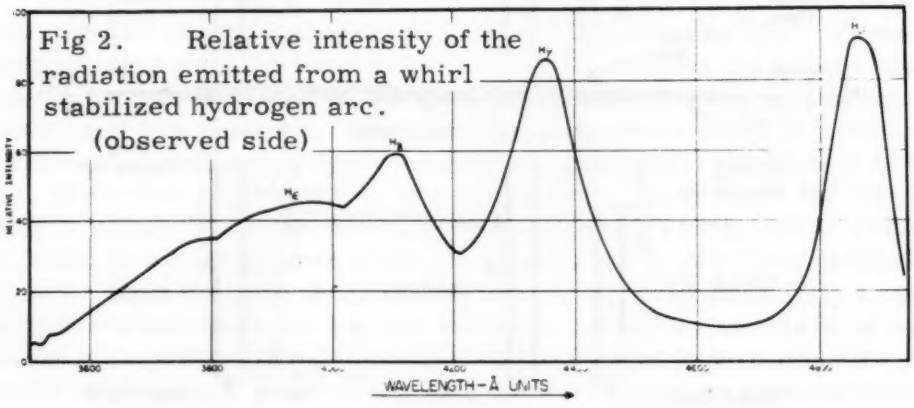

Fig 2. Relative intensity of the radiation emitted from a whirl stabilized hydrogen arc. (observed side)

fully ionized. A very strong continuum due to free-free and free-bound transitions is observed in the spectrum (Fig 2). The Balmer

lines appear strongly broadened. The last discernable line of the Balmer spectrum is the H-epsilon line.

It is planned to further increase the temperature of this plasma by the sudden discharge of a capacitor bank and to extend the spectroscopic methods to higher temperature ranges.

In the extensive experimental work resulting from the design of the vortex stabilized hydrogen arc, several interesting phenomena have been unveiled which could be worthy of detailed investigations. There are, for instance, the processes at the electrodes which are not yet understood beyond doubt. To sustain a direct current through a gaseous medium, a certain emission rate of electrons from the cathode is needed. Two different mechanisms of emission of electrons from a metal surface are known, thermionic and field emission, which may exist simultaneously. Quite a number of theoretical approaches have been suggested to explain the emission process in an arc discharge, but to date no satisfactory agreement with experimental data has been reached.

METAL CHELATES YIELD TO GAS CHROMATOGRAPHY

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Metal coordination compounds have long held the scientific interest of many investigators, but only recently have they begun to attract interests oriented toward practical applications. Utilization of these metal chelate compounds in the fields of optical lasers, vapor phase metal deposition, and ultrapurification of semiconductor materials is a representative sampling of the broad spectrum of new possibilities for these compounds.

Along with the current widespread interest in metal complexes came a need for a more accurate and convenient method for their analysis, separation, and purification. This problem has been under study by Lieutenants B. W. Ponder and R. W. Sievers, and Dr. R. W. Moshier of the Aeronautical Research Laboratories.

The resounding success for gas phase chromatography in the field of Organic Chemistry led to an investigation of this method

as a new approach to the analysis of the metal chelates. The low vapor pressure of most inorganic complexes does not make them readily adaptable to analysis by gas chromatography, since the high temperatures required for their elution usually accomplishes thermal degradation. However, it was felt that a proper investigation and evaluation of some of the variables involved might reveal conditions for a successful gas chromatographic analysis of these chelates.

The first step was to check out a number of complexes to see if they could be eluted without thermal degradation. Metal chelates of 2, 4-pentanedione were tried first because they are convenient to work with and are reasonably volatile as far as metal chelates are concerned. Most of the compounds were prepared by conventional means and were purified by recrystallization or vacuum sublimation. In some instances it was necessary to prepare the compounds in nonaqueous solutions.

Two types of gas chromatographic equipment were used in this study: a Burrell Model K-2 and a Burrell Model K-7. The Burrell K-2 is equipped with a thermal conductivity type detector and helium was used as the carrier gas. The column was held at constant temperature in some cases, while in others it was programmed manually up to a maximum of 300°C. The Burrell K-7 is equipped with a more sensitive thermionic emission type ionization detector. This unit has a separate flash vaporizer, and the column can be held at constant temperature or automatically programmed at any desired rate up to a maximum of 500°C.

Three types of columns were used. A glass column, one-quarter inch in diameter and 1 meter long, was packed with micro-glass beads which had been coated with 0.5% by weight silicone grease. A second column, made of 3 mm. stainless steel, was 3 meters in length and was packed with powdered teflon coated with 5% by weight Apiezon L grease. A third column was made of one-quarter inch glass tubing, was 3 meters in length, and was packed with powdered dextro quartz. Column temperatures ranged from room temperature to 250°C.

It was found that several of the chelates of 2,4-pentanedione came through the column unscathed at temperatures well below

their boiling points. Acetylacetonates of beryllium (II), aluminum (III), copper (II), iron (III), vanadium (IV), and chromium (III) have been eluted without thermal decomposition. Attention was next turned to the tri- and hexafluorinated derivatives of acetylacetone, since these were suspected to be more volatile than the unsubstituted analogs. Beryllium (II), aluminum (III), cobalt (III), zirconium (IV), and hafnium (IV) chelates of trifluoroacetylacetone and chromium (III), iron (III), copper (II), and rhodium (III) complexes of hexafluoroacetylacetone have been successfully eluted from the column. It was found that the chelates of the fluorinated β-diketones are much more volatile than the corresponding complexes of acetylacetone and can be eluted at a much lower column temperature. In some cases, a rapid elution at room temperature was observed. This striking increase in volatility in going from the acetylacetone complexes to the fluorinated complexes may be attributed to a combination of the decrease in intermolecular hydrogen bonding and intermolecular repulsion resulting from the incorporation of a shell of highly electronegative fluorine atoms in the periphery of the molecule.

By the use of these fluorinated derivatives, several mixtures of the metal chelates have been successfully separated and analyzed. A typical example is the separation of aluminum (III), chromium (III), Rh (III), and Zr (IV) chelates of trifluoroacetylacetone at a column temperature of 135°C.

The use of gas chromatography in the separation of geometrical and optical isomers is also under investigation. The conventional method of liquid-solid chromatography on an alumina column which has been used in the past is very tedious and time consuming. The preliminary results which have been obtained on the separation of the cis and trans isomers of tris - (1, 1, 1-trifluoro-2, 4-pentanedionoto) chromium (III) by gas phase chromatography are very encouraging. Although a clean cut separation of the isomers was not observed on the silicone grease column, their elution peak was split, indicating that some separation between the cis and trans isomers had been achieved.

If optically active substrates are employed as column packings, it should be possible to separate optical as well as geometrical isomers by gas-solid or gas liquid chromatography. If a solid, such as powdered dextro quartz is used, the basis of the separation is the difference in the rates of absorption and desorption of the d and l

isomers on the surface of the quartz. In gas liquid chromatography, where the column packing is on inert solid coated with an optically active liquid, the basis of the separation is the difference in solubility of one isomer in the liquid phase as compared with the other isomer. Using a dextro quartz column 12 feet in length, a partial resolution of d, l chromium hexafluoroacetylacetonate has been achieved. With the column at 55°C, an early fraction showed an apparent molecular rotation of +1600° ± 300° at the sodium D line.

In summary, the gas chromatographic route looks very promising as a method for the analysis, separation, and purification of metal chelates. It may also prove useful as a means of separating cis and trans isomers of the unsymmetrical chelates, and of resolving d, l isomers. Gas chromatography also looks good as a way to purify metal containing compounds. A preliminary account of the above work has appeared recently in Chemical and Engineering News, 40 No. 14, 50 (1962).

Ferromagnetism

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Directorate of Physical Sciences (AFOSR)

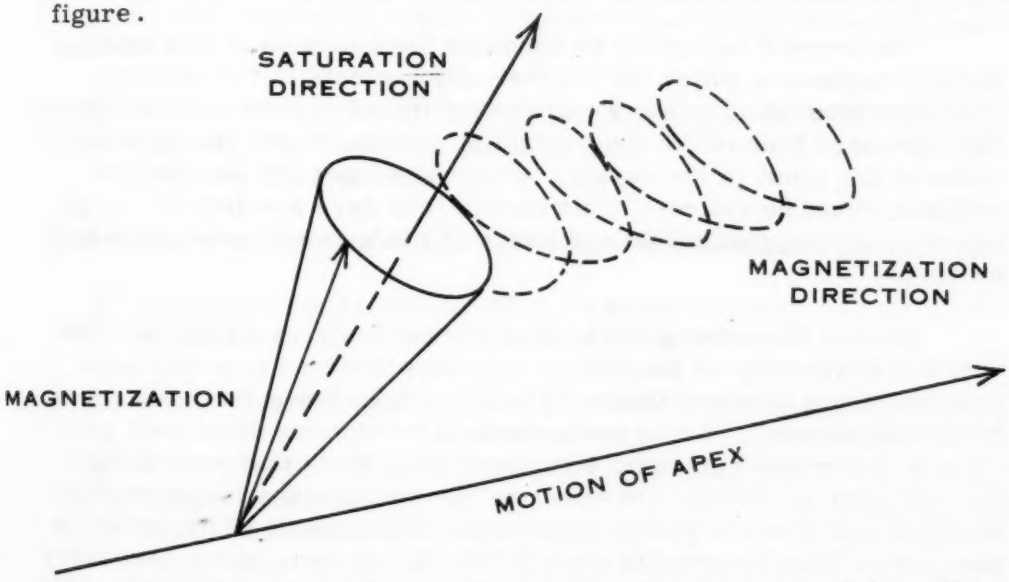
Magnetic materials have found many diverse applications in technology of the weapon systems of the Air Force. And these applications are increasing at an exponential rate as new methods and techniques of preparing materials with special magnetic properties are found. In order to provide guidance for the selection of materials and to find the limitations for different classes of materials, theoretical and experimental studies of the fundamental mechanisms of ferromagnetism, ferrimagnetism, and anti-ferromagnetism are required.

One of these mechanisms is the origin of the internal, effective magnetic fields of the order of 1,000,000 gauss in the transition metals such as nickel, iron, and cobalt. This origin was not understood until in 1928 Heisenberg proposed a model of ferromagnetism based on the then new quantum mechanics and the exclusion principle.

The solution to Heisenberg's model and the determination of the temperature variation of the spontaneous magnetization has been investigated by many authors since that time. Their names read like a who's who in theoretical physics: Bloch, Holstein, Van Kranendonk, Bethe, Dyson, and others. These investigations revealed that the magnetization decreases as the three-halves power of the temperature at low temperatures (below that of liquid nitrogen), and that there is a divergence of opinion as to what happens at higher temperatures.

This divergence arises from the different methods of estimating the violence of the collisions, or the rate of decay, of the approximate solutions of Heisenberg's model. A simple analog of these methods and solutions is contained in the treatment of the propagation of electromagnetic energy along a slightly-lossy transmission cable. The approximate solutions of Heisenberg's model correspond in the analog to the propagation of electromagnetic energy along a perfectly loss-free transmission cable.

These approximate solutions, which are called spin-wave states, give rise to a magnetization field at some instant of time as shown in figure.



It is seen that the magnetization lies on a cone and describes a uniform spiral in the crystal. The opening angle of the cone has been exaggerated in the figure for illustration purposes. An angle on one-millionth of a degree would be considered large!

The two methods of estimating the decay of these spin-wave states have their analogs in the propagation of a continuous, single

frequency electromagnetic wave and in the propagation of a short puls electromagnetic energy respectively.

The first method is to consider two spirals of figure 1 as being simultaneously present. These two spirals will then deform one another and will disappear after a finite length of time just as an electr magnetic wave decays in a cable. This deformation has been treated in two papers by Dyson who concludes that the deformation is small and gives rise to a small correction term for the spontaneous magnet zation which is of the fourth power of the temperature.

Dyson's papers, unfortunately, were not intelligible to a majori of the solid state physicists due to the formidable mathematics contained. Frederick Keffer at the University of Pittsburgh under Air Force Contract AF49(638)-323 was able, however, to express the mathematical formulae of Dyson's papers in terms of plausible physical arguments and was able to derive the results using very simple ideas.

The second method is to consider the collision of two small, moving regions in which the magnetization points in the opposite direction from the remainder of the saturated crystal. On the basis that the magnitude of the magnetization cannot exceed the saturation value at any point in the crystal, physicists have argued that the collision must be violent. This should then have a relatively large effect on the magnetization and hence Dyson's result must contain an error.

Newton Greenberg, under Air Force Contract AF49(638)-399 with the University of Maryland, has reconsidered this collision process in his doctoral thesis "Theory of Spin Wave Interactions in Ferromagnetism". Using mathematical techniques developed previously under this contract, Mr. Greenberg finds that even though the collision is violent, its effect on the spontaneous magnetization is small and Dyson's result is correct. This result is important in that, while Dyson's results were felt to be correct, some necessary approximations were made which could not be checked directly. Now, starting from an entirely different viewpoint, the same results have been obtained, cross-checking those of Dyson.

This study is a part of the program of the Solid State Sciences Division to learn more about the fundamental nature of the magnetization processes in the solid state.

notice to our readers

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